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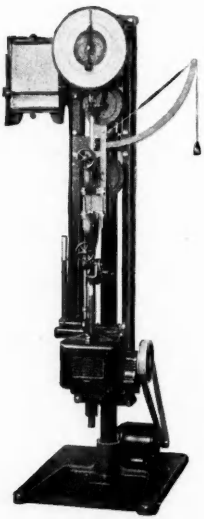

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Cellulose Orientation, Strength and Cell Wall Development of Cotton Fibres*

By DR. EARL E. BERKLEY †

Summary

THE possible effects of thin-walled, or so-called "immature," fibres on the precision of the X-ray method for estimating the tensile strength of raw cotton have been studied and are reported in this paper.

The materials were obtained, for the most part, from a cotton field of the North Carolina State Experiment Station at Raleigh, during the summer of 1937. Cotton flowers were tagged on the day of opening and the bolls were collected periodically. In the X-ray studies, four different series of samples from Mexican Big Boll cotton and one each from Hopi and Sea Island cottons have been used. The samples were taken at daily intervals during the period of fibre elongation and until after secondary thickening was initiated and at one to five day intervals up to 45 days and a final sample after the bolls opened.

Tensile strength, and per cent thin walled fibres were determined on a limited number of samples selected from the several series of the Mexican Big Boll cotton.

Measurements of the 002 rings of the X-ray diffraction patterns of the fibres containing primary wall only, showed a tendency for preferred orientation of the b-axis of the unit cell, *i.e.*, the long axis of the cellulose molecules, transverse to the fibre axis. Microscopic studies under polarized light also showed that the cellulose of the primary wall lies transverse to the fibre axis.

* This study is a part of the program of Cotton Quality and Standardization Research under the direction of Dr. Robert W. Webb, and was reported at a meeting of the Cellulose Division of the American Chemical Society at Milwaukee, Wis., Sept. 6, 1938.

† Associate Cotton Technologist, Bureau of Plant Industry and Agricultural Marketing Service, U. S. D. A.

As the secondary wall was laid down, the 002 ring of the X-ray diffraction patterns became equally dark throughout, and with continued deposition of cellulose the region of greatest darkening of the ring shifted 90 degrees from that of the primary wall. In one series of samples the patterns showed a gradual change from the condition of transverse arrangement of the cellulose in the primary wall through an intermediate stage to a more parallel arrangement in the secondary wall. The other three series of Mexican Big Boll cotton showed rather abrupt changes; that is, the transverse arrangement was pronounced on one day, whereas on the following day parallel or spiral arrangement was noted.

What could be interpreted as random orientation of the cellulose was not observed in any of the six series of samples at any stage of development. The apparent random orientation reported in one series was due to the superimposition of layers of differently oriented cellulose in the primary and secondary walls.

The "wax" pattern was more prominent than the cellulose pattern during the stage when the cell contained only the primary wall. Preferred orientation, with the long axis of the wax molecules transverse to the fibre axis, was indicated by prominent rings in the wax pattern. These waxy substances were readily extracted from the Mexican Big Boll cotton with alcohol but slowly, if at all, with chloroform or carbon tetrachloride.

The cellulose pattern of the primary wall and the wax pattern both disappeared (became too thin to be differentiated from the background) within 4 to 6 days after secondary thickening was initiated.

The secondary wall pattern changed gradually with cellulose deposition for the first few days, showing a more or less progressive improvement of the orientation of the successive layers of cellulose in relation to the fibre axis. However, little or no improvement in the orientation, as shown by the X-ray pattern, was observed after about the 6th day.

The tensile strength of the fibre, as measured by the improved Chandler bundle method, increased for 12 to 18 days after secondary thickening was initiated, and reached its maximum at about the 35th day after the flowers opened, or 3 to 4 weeks before the bolls opened.

During the first 30 to 35 days after flowering, or 12 to 18 days after secondary thickening began, the strength obtained by the Chandler method and that calculated from the X-ray data do not agree, but, since they agree throughout the later stages of development, it is indicated that the proportion of ordinary thin walled fibres, which usually occur in commercial cottons, will not affect the application of the X-ray method for the purpose of strength estimation or prediction.

Introduction

IN the Cotton Technological laboratories of the Agricultural Marketing Service, a study is being made of an X-ray technique with a view to developing a more rapid and practicable method for determining the strength of raw cotton. There are urgent needs for an improved method to determine strength in connection with cotton quality standardization and classification as necessitated by marketing problems on the one hand, and by breeding and production problems on the other.

Attention has been called to the X-ray diffraction method as a tool, for cotton quality differentiation by Clark, Pickett and Farr,[6] who, through a cooperative study, observed that the degree of preferred orientation of the cellulose in three different samples was associated with the quality of the cotton.[a]

The general features of the X-ray method for estimating the tensile strength[b] of raw cotton, based on the relation of strength to degree of alignment of the cellulose with the long axis of the fibre, have been described by Sisson[18] on the basis of studies conducted by him in the Bureau's laboratory or through cooperation as a Collaborator of the Bureau of Agricultural Economics while a Textile Foundation Fellow at the University of Illinois. Improvements in the X-ray method and a description of a new microphotometer for measuring the X-ray patterns have been presented by Berkley and Woodyard.[4] Conrad and Berkley[7] recently discussed the X-ray method in relation to the spirality of the cellulose in the fibre and outlined some of its possibilities and limitations.

Although a good correlation has generally been found to exist between the fibre structure and the strength of cotton, occasional samples have been encountered where an appreciable difference occurred between the observed and estimated strengths. Such discrepancies might be sought in (a) the strength data; (b) the X-ray technique; (c) possible effects of the thin-walled, or "immature" fibres, either through the cellulose pattern from the primary wall, or through the wax pattern; (d) deterioration of the cotton by microorganisms; or (e) effects of light or other agencies.

Careful examination of the strength values as determined both by the improved Chandler bundle method and by the X-ray method showed that most of the discrepancies between the two values cannot be accounted for by the techniques used.

[a] Mrs. Farr was, at the time, a member of the cotton technological staff, Bureau of Agricultural Economics, U. S. Department of Agriculture.

[b] The observed tensile strength values considered in this paper were obtained by the improved Chandler bundle method.[10]

Under certain conditions the X-ray pattern of the cellulose of the primary wall may be a source of error in the measurements. However, this factor would not appear to be a disturbing one if the cellulose of the primary wall showed random orientation as reported by Sisson.[19] On the other hand, if the cellulose of the primary wall lies transverse to the fibre axis, as indicated by the microscopic studies of Levine,[14] Balls,[3] Anderson and Kerr,[2] and Wergin,[21] the X-ray-strength relationship might be affected.

Also, Gunderman, Wergin and Hess [8] identified two wax rings in patterns of young fibres which fall on opposite sides of the 002 ring of cellulose. According to Wergin,[20] and Hess, Trogus and Wergin,[9] these rings may completely hide the 002 cellulose ring at certain stages of growth. Thus, if the waxes occur in sufficient quantities to show in the X-ray patterns of samples of commercial cottons, they, too, may affect the photometer readings and thereby cause distorted values for the estimated strengths.

Appreciable errors due to the cellulose and wax patterns of the primary wall would not, of course, be expected to occur unless there is a preponderance of thin walled fibres in the sample, since the primary wall makes up a very small proportion of the average fibre. The general run of commercial and experimental samples of cotton tested in the Bureau's laboratories have been found to possess, on the average, about 30% thin walled fibres. Wide deviations, however, have been noted from sample to sample and occasional ones have been found which contained 75% or more of thin walled fibres.

In the light of the foregoing, it seemed desirable to determine the effects of each factor on the X-ray-strength relationship. The easiest and best way of doing this and, at the same time, of obtaining a better understanding of the overall fibre structure was considered to be by conducting some special studies, beginning with very young cotton fibres when the structure is relatively simple, and following the structure and strength, layer by layer as the cell wall is laid down.

This paper represents a progress report covering observations on thin-walled fibres and on the arrangement of the cellulose and so-called "waxes" of the primary wall,* and suggesting their possible effects on the precision of the X-ray method for estimating the strength of raw cotton. Changes in the secondary wall as the different layers of cellulose are laid down, and certain preliminary data on the strength and other physical properties of the fibres, are included and discussed. Although additional studies are in progress with respect to the effects of thin-walled mote fibres, biological decay and chemical disintegration, on the precision of the X-ray method as a tool for cotton quality research and testing, no results are included in this paper.

Materials and Methods

The samples used in this study were for the most part young or immature fibres from unopened bolls of known age. They were collected by the author during the summer of 1937, from plants growing in the Experi-

* "Primary wall," as described by Anderson and Kerr [2] and referred to in this paper, is intended to mean the outer sheath of the cotton fibre or the portion of the wall formed as the fibre elongates. "Secondary wall" refers to that portion of the cell laid down within this outer sheath after the fibres cease to elongate appreciably. The secondary wall usually consists of a number of concentric layers of cellulose in line with the observations reported by Balls [3] and Kerr.[11]

ment Station fields at Raleigh, N. C.† The major portion of the work was carried out on Mexican Big Boll cotton, a variety of *Gossypium hirsutum L.* Varieties of two other species were also examined, *i.e., G. barbadense L.* (Seabrook Sea Island) and *G. hopi Lemton* (Hopi cotton), The X-ray studies were conducted at Washington, D. C.

The age of the fibres as collected in the field was determined by tagging the flowers on the day of blooming and then collecting the bolls on successive dates in such a manner as to give material of the desired age. It is appreciated from the work of Lang[13] that all of the fibres may not be initiated on the first day of flowering; however, since a large percentage of them are, the age of the fibres may be considered for this discussion as beginning on that date. Three different groups of flowers were tagged on the Mexican Big Boll plants during the summer of 1937, one on July 20, a second on July 26 and 27, and a third on August 3.

Preparation of the X-ray Samples

Five to ten bolls of Mexican Big Boll, Hopi, or Sea Island cotton, were selected for each periodic sample. The bolls were opened immediately on being brought to the laboratory and the locks dropped into boiling water for a few minutes to untangle the fibres so that they could be paralleled. This was found to be necessary in all samples that coalesced on drying and where secondary thickening had not progressed far enough to give the fibres sufficient strength to withstand the combing process.

The fibres were paralleled by combing carefully under a stream of water on a glass plate. The seed was placed on a glass plate (a lantern slide cover glass is a convenient size) and a stream of water played on it until the fibres were spread out. The seed was held in place, while the fibres were being combed, by means of a dissecting needle run through it and held in the same hand as the glass plate. The plate was tipped slightly to one side, and the fibres washed to the large or chalazal end of the seed. A second dissecting needle was used to remove the larger tangles before applying the combs. In the case of long fibred cotton, as for example Sea Island cottons, the ends of the fibres were clipped off about one inch from the seed, thus removing a large percentage of the tangles which, if an attempt had been made to comb them out, would have resulted in a loss of fibres. Two combs, a coarse one with about 32 teeth per inch, and a fine one with about 64 teeth per inch, were used. For convenience, sections of the combs about one inch in length were mounted on handles in the form of miniature rakes. The fibres can be carefully observed against a dark background while being combed if a relatively bright light is focused on them. In this way tangles are visible and it is easy to see when the fibres are paralleled.

Before secondary thickening began the fibres were easily paralleled after the boiling water treatment, but they became progressively more difficult to handle and parallel as the wall thickness increased, due for the most part to tangling of the long fibres. After secondary thickening had progressed five to ten days it was possible to parallel the fibres

† Appreciation is extended to members of the staff of the Bureau of Plant Industry field station at Raleigh, N. C., for assistance with the tagging of flowers and the collection of samples, for valuable suggestions on the preparation and handling of the materials, and for weather observations during the period of growth of the fibres.

without first boiling them in water, but, regardless of how it was done, the combing process at this stage was laborious. When it was not convenient to comb the fibres immediately, they were collected and boiled for a few minutes in water and then preserved in alcohol until used. In all cases where fibres that would coalesce on drying were used it was necessary to boil the fresh material in water before preserving it and to comb the fibres under running water in order to be certain of their alignment.

Once paralleled the fibres were either dried, suspended vertically between a dissecting needle at one end (placed through the seed or bundle of fibres) and a filter paper at the other, or chemically treated and then dried in the same manner. The ends of the fibres matted on the filter paper which served to hold the bundle and prevent kinking and twisting. As the fibres shrank on drying the filter paper remained attached, but only the tension resulting from the weight of the paper was applied to the fibres and this was negligible.

It was necessary to extract certain samples with organic solvents in order to remove the waxes or non-cellulose materials responsible for the extraneous rings in the X-ray pattern of the young fibres. Numerous treatments were tried, including extraction with chloroform, carbon tetrachloride, ether, benzol and alcohol and mixtures of benzol and alcohol.

The very young fibres gave very faint and indefinite patterns until they were given an alkali boil. The samples in the form of bundles were boiled anywhere from a few minutes to several hours in 1, 2, or 6% sodium hydroxide solution. The samples were washed in hot water and rinsed in a dilute solution of acetic acid in order to remove the caustic. A solution of about 0.1N hydrochloric acid was used alternately with the alkali boils on a few samples in an attempt to separate the fibres after they had dried into a horny mass.

The X-ray diffraction patterns were obtained from bundles of cotton fibres about one millimeter in diameter using Copper Kα radiation. The films were developed under controlled conditions, and certain ones measured.

Samples for Strength and Other Physical Tests

A number of bolls of the Mexican Big Boll variety were selected at frequent intervals as early as the fibres could be dried without coalescing into a horny mass, for strength determinations. The first sample was taken at 20 days after flowering and the last one after the bolls opened. One lock was removed from each boll and preserved in alcohol. The fibres from the other locks were dried on the seeds by placing the seed cotton in a tray in a warm place where the air was blown over it by means of an electric fan. It was frequently stirred and separated to promote drying.

When air dry, the fibre was carefully removed from the seed by hand to avoid excessive breakage, and thoroughly mixed in preparation for the tests. Unfortunately, the fibres of the 20-day sample contained a sticky material on the surface which prevented combing and preparation of Chandler bundles; therefore, no tests were made on this sample. The 23-day and later samples were tested for tensile strength, and per cent thin-walled fibres, in the physical testing laboratories of the Cotton Quality and Standardization Research Section of the Agricultural Marketing Service, according to the procedures described by Richardson, Bailey and Conrad [16] and in the A.S.T.M. Standards on textile materials.[1] Also,

cross-sections were made and photographed, to show degree of cell wall development at each age, according to the method described by Karrer and Bailey.[10]

Representative portions of these samples were used also to prepare bundles for the X-ray method. X-ray patterns were recorded and measured according to the method described by Berkley and Woodyard.[4] The calculated or X-ray strength was obtained by substituting the 40% angle, A, in the equation $S = 193.5 - 3.19A$, where S = strength.

Results

Orientation of the Cellulose in the Primary and Secondary Walls.— When the fibres, containing only primary walls or those in which the secondary thickening had not progressed more than about five days, were dried in the form of small bundles, the individual fibres united in one thread-like strand. They were tightly packed and glued together by the hardening of their gelatinous surfaces so that the mass formed a rigid structure. The individual fibres did not readily separate from each other after boiling for hours in water, 0.1N hydrochloric acid, 6% sodium hydroxide or an organic solvent such as alcohol, benzol, chloroform or carbon tetrachloride. Even an alternation of treatments in dilute hydrochloric acid and 6% sodium hydroxide failed to separate them, unless the bundles were crushed or the fibres were teased apart.

Immediately after secondary thickening began, the thread-like bundles tended to twist on drying, and when they were about four to six days older the individual fibres ceased to unite and it was possible to obtain an ordinary loose bundle of fibres. At this stage the individual fibres, after collapsing to form ribbons, convoluted and became kinky on drying. The fibre bundles shrank appreciably in length upon drying, particularly those bundles representing only the primary wall, some of which appeared to lose from one third to one half of their original lengths.

X-ray diffraction patterns of young cotton fibres, before the secondary thickening was initiated, showed that, for the three species studied, the long axis of the cellulose chains lies predominantly transverse to the long axis of the fibre. Close inspection of the 18- and 19-day patterns of Fig. 1, and also pattern b of Fig. 2 will show that the 002, $10\bar{1}$ and 101 rings * are densest to the right and left of the patterns,† indicating that although it is not highly preferred, there is a definite tendency for orientation of the b-axis of the unit cell in a direction perpendicular to the fibre axis.

The X-ray patterns in Fig. 1 represent a portion of the samples from the July-20 tagging of the Mexican Big Boll cotton. The other three series from this variety and those from the Hopi and Sea Island cottons also showed transverse arrangement of the cellulose in the primary wall, although they did not show the intermediate stage represented by the 20-day pattern.

The circular plots of the opacity of the 002 rings just beneath each pattern are arranged with the respective parts of the plot for each sample in the same relative position as in the pattern. It may be observed, both

* These are respectively the densest ring and the two inner rings prominent in the patterns.

† For convenience the X-ray diffraction patterns shown in the figures of this paper are arranged with the long axis of the bundle of fibres horizontal to the page.

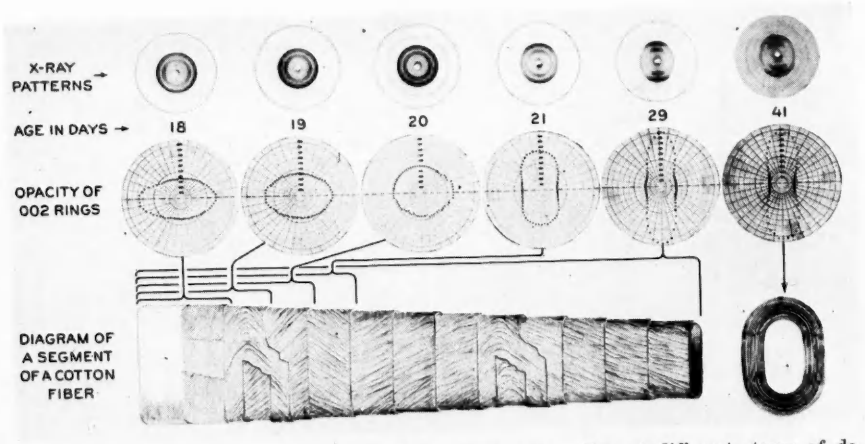

FIG. 1. The arrangement of the cellulose of the cotton fibre at different stages of development as shown from X-ray diffraction patterns of Mexican Big Boll cotton. The plots indicate the blackening of the 002 rings of the patterns and therefore the arrangement of the cellulose. The diagram indicates the writer's interpretation of the lamination of the cell wall and the spiraling of the cellulose in the different layers.

from the patterns and the plots, that the arrangement of the cellulose changed somewhat gradually from the transverse arrangement observed at 18 days, through a condition which could be interpreted as random arrangement at 20 days, to the usual cotton pattern at 29 days. A microscopic examination of the samples under polarized light, using a Selenite plate also showed the cellulose of the primary wall to lie transverse to the axis of the fibre. Soon after secondary thickening began, the primary wall was completely compensated by the spiral cellulose of the secondary wall and no further detail on the structure could be obtained readily by this means.

Secondary thickening first appeared on the 19th day, as shown by microscopic examination in ordinary light after staining the fibre in chlorozinc iodide. Only a portion of the fibres showed secondary deposits at that time, however, and the transverse cellulose of the primary wall was dominant in the X-ray pattern. On the 20th day, secondary thickening was more pronounced, as indicated by a microscopic examination, but it had not started in all cells. The more or less equal distribution of density around the 002 rings of the X-ray pattern at 20 days indicates that there was just sufficient cellulose deposited in the secondary wall so that its pattern, when superimposed on the pattern of the primary wall, gave equal density throughout the rings. This can best be understood by considering the diagram in Fig. 1.*

It may be of interest to note here that the 20-day sample represented in Fig. 1 is the only specimen of cotton fibre observed to date whose pattern showed approximately equal density all the way around the 002 ring. Twenty-four hours later, at 21 days (see Fig. 1), the secondary wall had become dominant, as shown by a 90-degree shift of the pattern, placing the greatest blackening of the 002, $10\bar{1}$ and 101 rings at the top and bottom of the pattern. This shows that the preponderance of the cellulose was at that stage more nearly parallel with the fibre axis. Two days later (23 days after flowering) the fibres gave a typical cotton pattern, and after about ten days of secondary deposit no consistent changes were observed in successive patterns (compare the 29- and 41-day patterns in Fig. 1).

Due to the blending of the primary and secondary wall patterns, both of which were visible during the first two or three days after secondary thickening began, it was difficult to determine the exact nature of the secondary wall pattern. The primary wall pattern gradually disappeared and the secondary wall pattern became prominent. As the secondary wall pattern became established, the arcs, particularly from the 002 plane, became shorter. This was due in part to the fact that the primary cell wall gradually assumed smaller proportions in relation to the total with the consequent disappearance of its pattern. After the primary wall pattern had practically disappeared, the 002 arcs from the secondary wall were long (see 21-day pattern of Fig. 1), which indicates that the long axis of the cellulose chains of the first layers of the secondary wall are laid down with a greater spiral angle with respect to the fibre axis than are those of subsequent layers.

For purposes of illustration, the drawing in Fig. 1 is made with the cellulose (represented by the branching system of shading lines) spiraling in opposite directions for the first four layers of the secondary wall. This reverse spiral in adjacent layers is not necessarily characteristic of the entire

* The drawing is patterned after that of Anderson and Kerr [2] with certain modifications.

or not the waxes could be readily removed from them with these same solvents.

After the Mexican Big Boll samples were treated in chloroform or carbon tetrachloride, the wax patterns became diffuse and often disappeared temporarily, but when the samples were again treated in alkali, the wax patterns reappeared and were often more intense than those from unextracted samples.

Thus, for the cotton fibres representing the three species studied, and under the conditions described, it was observed that both the wax and the cellulose patterns of the primary wall showed preferred orientation with the long axis of the molecules transverse to the fibre axis. As the secondary wall developed, the wax pattern and the cellulose pattern of the primary wall gradually disappeared (Fig. 3) and, as the wax pattern dis-

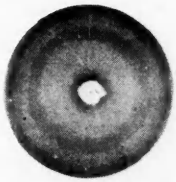

FIG. 3. X-ray diffraction pattern of an untreated bundle of fibres approximately 24 hours after secondary thickening began. The short dense ares at the equator are from the wax pattern, whereas the cellulose pattern of the secondary wall is prominent at the poles. (Fibre axis, horizontal.)

appeared, the ares (see dense lines at equators) became shorter. The alkali treatment, used to remove the amorphous haloes and intensify the cellulose and wax patterns before the secondary wall developed, failed to bring out either of them after secondary thickening had progressed five to six days. This may be explained by the fact that the primary wall becomes a smaller percentage of the fibre and of the sample as the fibres thicken, thus making the patterns so indefinite that they can no longer be differentiated from the background fog. There is considerable evidence from the data presented in this paper, and from a study of thin walled fibres from open bolls, that the waxes do not increase appreciably as secondary thickening proceeds. Chemical analysis will, therefore, probably show little or no more wax per fibre in mature cotton than in very young fibres.

Certain Fibre Properties at Progressive Stages of Development.— The results of the fibre analyses and X-ray measurements on the dried samples of Mexican Big Boll cotton are shown in Table I, arranged according to date of tagging of the flowers and age of the fibre after flowering.

The number of days after flowering before secondary thickening occurred was determined by daily microscopic examination of the fibres during the period when it was likely to begin. This time varied slightly for the three series included. The number of days after secondary thickening began is shown because it is considered to be a better index of the wall development than the days after flowering.

fibre. In fact, the convolution of the fibre and the uniformity of the orientation of the cellulose, after the first few layers are deposited, suggests that the spiral may be in the same direction for all succeeding layers after the first two or three, as suggested by Anderson and Kerr.[2]

So-Called "Wax" Pattern of the Cotton Fibre.—The X-ray patterns, illustrated in Fig. 1, were obtained from bundles of fibres that had been extracted with organic solvents to remove the constituents responsible for the non-cellulose or wax patterns, and boiled in 6% sodium hydroxide to intensify the cellulose patterns. Pattern a, of Fig. 2 from a bundle of fibres which had been treated in boiling 6% sodium hydroxide and hot 0.1N hydrochloric acid alternately, shows the wax rings overshadowing the 002 ring of the cellulose pattern. It will be observed that the wax pattern (see dense ring) shows preferred orientation and, as will be shown later, the rings corresponding to the 4.14 Å spacing indicates that the long axis of the wax molecules lies transverse to the long axis of the fibre, *i.e.*, parallel to the cellulose of the primary wall. All of the samples examined in this study, including three species of cotton, that gave the non-cellulose, or wax pattern, showed strong diffraction rings from planes perpendicular to the fibre axis.

Pattern b, of Fig. 2 was made with the same bundle of fibres as pattern a, the only difference being that it had been extracted with an alcohol-benzol mixture for approximately 4½ hours and soaked over night

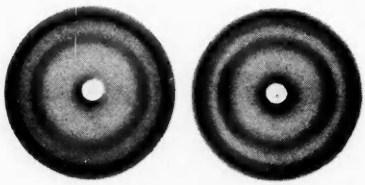

FIG. 2. X-ray patterns of a bundle of fourteen day-old fibres: a, non-cellulose rings obscuring the 002 ring of cellulose after a number of alternate treatments in boiling 6% NaOH and hot 0.1N HCl; b, cellulose pattern of the same bundle of fibres after removal of non-cellulose constituents with a mixture of alcohol and benzol. Note the greater density in each pattern of the darker ring at the equator, showing preferred arrangement of both the wax and cellulose constituents, transverse to the fibre axis. (Fibre axis, horizontal.)

in the solvent. The cellulose pattern is clear in b, with no trace of the wax pattern left. When alcohol or a mixture of alcohol and benzol was used to remove the wax, no trace of the pattern could be detected thereafter regardless of the succeeding treatments. It was observed, on the other hand, that extractions in chloroform or carbon tetrachloride for periods up to 72 hours did not remove the waxes or non-cellulose materials responsible for the pattern in the Mexican Big Boll cotton. Since the samples of Hopi and Sea Island cotton reported in this paper were not extracted with chloroform or carbon tetrachloride, it is not known whether

The per cent thin walled fibres, Table I, was relatively high in the younger samples of each series. It decreased rapidly until about the 35th day and more gradually thereafter (see Fig. 4). The free-hand curve drawn through the points in Fig. 4 shows the period of rapid elongation before secondary thickening begins, the rapid change in cell wall thickness between the ages of 25 to 35 days, and the final period of little or no change. From microscopic examination, it seems probable that the thick walled fibres appearing before the 26th day are fuzz fibres. The relatively low percentages of thin walled fibres present at or near the end of the series approaches that of the average of 30% ordinarily found in commercial samples.

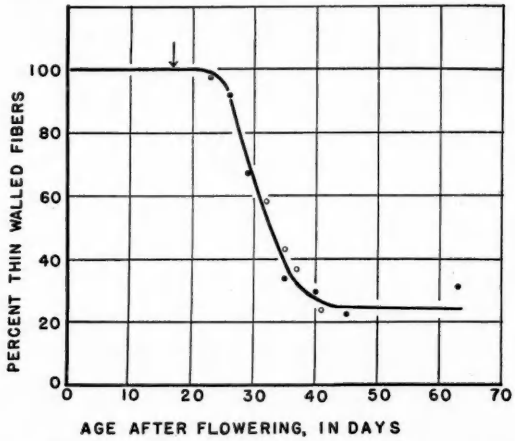

FIG. 4. Proportion of thin-walled fibres present at different ages. The shaded circles represent the series tagged on July 26 and 27, the open circles those tagged on July 20 and the half shaded circle (at 23 days), the single sample tagged on August 3. The arrow indicates the approximate age when secondary thickening started.

The 40% angle measured on the X-ray patterns of the different samples is shown in the sixth column of Table I. With the aid of the regression equation, referred to previously, the estimated, or X-ray strength, shown in the seventh column, was obtained. As contrasted with the observed strength, column 8, of Table I, the X-ray method indicated essentially the same strength for all the samples, irrespective of age or series.

Because fibres containing only primary wall, or those in the early stages of secondary thickening generally matted and adhered to each other on drying, the tensile strength of the young cotton fibres could not be determined until seven days after the secondary thickening was first observed. Even when they did not stick together, they were too frail and weak to permit the preparation of bundles in the usual way.

As soon as the bundles could be satisfactorily prepared, tensile strength was measured and the results will be found in Table I. It is noted that

TABLE I

Certain physical properties associated with the ages or the degree of development of cotton fibres.

Date of flowering	Age of fibre	Occurrence of secondary thickening after flowering	Age of secondary wall	Thin walled fibres	40% angle	Tensile Strength	
						Estimated (X-ray method)	Observed (Chandler method)
	Days	*Days*	*Days*	*Percent*	*Degrees*	*1000 lbs/sq. in.*	*1000 lbs/sq. in.*
July 20	32	19	13	58.0	34.8	82.8	68.6
July 20	35	19	16	43.0	35.8	79.7	73.6
July 20	37	19	18	36.4	35.1	81.5	69.3
July 20	41	19	22	23.9	35.2	81.5	74.9
July 26	26	17	9	91.9	35.2	81.6	53.2
July 26	29	17	12	66.8	36.1	78.7	70.9
July 27	35	17	18	33.8	36.0	79.0	79.4
July 26	40	17	23	29.7	35.9	79.0	80.0
July 27	45	17	28	22.3	37.4	74.6	78.8
July 27	63*	17	46	31.4	34.8	82.8	82.6
August 3	23	16	7	97.7	35.6	80.3	56.0

* Open bolls.

the observed tensile strength increased rapidly with additional deposits of cellulose in the secondary wall and approached a maximum between the 12th and 18th days after secondary thickening began. This corresponds to 29 to 35 days after flowering, or 3 to 4 weeks before the bolls opened in the case of the series from the flowers tagged on July 26 and 27 and represented in Fig. 5. There were no appreciable increases or changes observed in the strength after this date,—the difference between values not being statistically significant. The samples from the flowers tagged on July 20 (see Table I) constitute a more limited series and, without the earlier stages, it is impossible to know precisely when the maximum strength was first reached. The differences in the values reported are relatively small and it is presumed that the maximum was first reached on or about the 13th day after secondary thickening appeared, which is the first observation recorded. One very interesting point to be noted in connection with the latter series is that the samples, even after they had reached maximum strength, were apparently weaker than those from the July 26 to 27 taggings.

The data in Table I indicate that in the July 20 series there were no significant variations in the observed strengths after the per cent thin walled fibres had dropped as low as 58%. In the July 26 to 27 series, maximum strength was reached when the percentage of thin walled fibres had decreased to 33.8%. However, the percentage of thin walled fibres was changing very rapidly at this period (Fig. 4) and when the strength is plotted against per cent thin walled fibres, Fig. 6, it is seen that maximum strength was reached already when there were approximately 50% thin walled fibres.

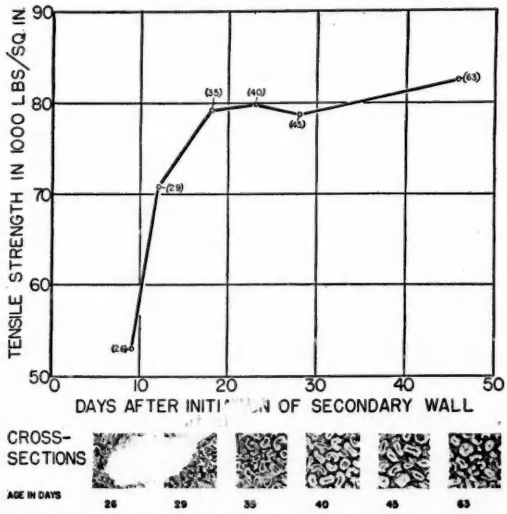

FIG. 5. Relation between the fibre cell wall development and the tensile strength of a series of samples of Mexican Big Boll cotton. The numerals in parenthesis, at the plotted points, indicate the age of the fibres in days after the flowers opened. The series of photomicrographs of the fibre cross-sections illustrates the relative thickness of the cell walls at the corresponding ages.

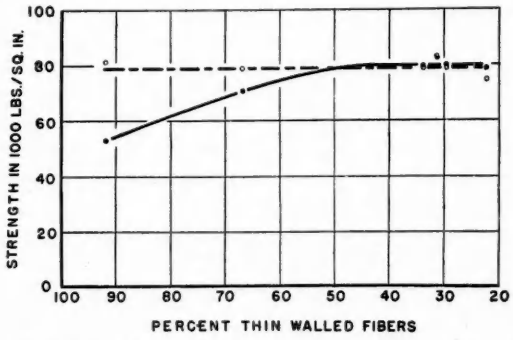

FIG. 6. Relation of observed (Chandler) and estimated (X-ray) strength to percentage of thin walled fibres. The solid line represents the values obtained by the Chandler bundle method, and the broken line those obtained by the X-ray method. The percentage of thin walled fibres decreases as the cotton approaches maturity. (See Table I.)

The fibre cross-sections shown at the bottom of Fig. 5 were made on representative portions from the samples used in making the strength tests. It will be of interest to note that, even though the cell walls were relatively thin at 35 days (18 days after secondary thickening began or 3 to 4 weeks before the bolls opened), the fibre-bundle strength had reached a maximum at or before this time.

Discussion

While it is recognized that the fibre strength data presented in this report are limited both in number of tests and varieties of cotton used, nevertheless certain interesting relationships are suggested. The observed strength rapidly increased and approached a maximum by the 35th day after flowering, or from 3 to 4 weeks before the bolls opened. No significant increase in strength was indicated by the data after the cotton reached a stage of development where there was approximately 50% thin walled fibres present.

On the other hand, the strength as calculated from the X-ray patterns, *i.e.*, the degree of alignment of the long chain cellulose molecules with the long axis of the fibre, was the same within the limits of experimental error at all stages represented in the strength series. The X-ray patterns from the cellulose and wax of the primary wall had completely disappeared before the stage represented by any of the samples on which strength determinations were made, and their effect on the X-ray-strength relationship could not be detected in the Mexican Big Boll cotton.

In the light of the evidence reported, it is apparent that the strength values obtained by the two methods agreed satisfactorily for the samples older than about 35 days. However, they did not agree for the samples younger than this. Thus, according to this study there was a period of not more than 15 to 20 days after secondary thickening began when the tensile strength of the cotton could not be estimated satisfactorily by the X-ray method. The exact age at which agreement would be expected for the usual run of cotton cannot be determined from these data alone, due to the natural biological variations to be expected and the probable effects of climatic conditions. However, the interval between the time when the fibre is initiated on the seed and that when the strength of the fibre, as indicated by the X-ray method, agrees with the strength, as shown by the improved Chandler bundle method, is not important from a practical point of view. The cotton grown on different plants or on the same plants at different periods during the year may not mature at the same rate, but it is unlikely that even so called "immature" cotton, as identified by classers or associated with the sledding process, would contain sufficient fibres of this character to affect the estimated strength.

The physical properties of the samples from the flowers tagged on July 20 were somewhat different from those of the fibres from the flowers tagged later. For comparable ages, the fibres of the July 20 series were found to be appreciably longer and coarser than those of the July 26 to 27 series. The mean length of the fibres from the July 20 tagging was 1.14 inches, whereas that of the samples from the July 26 and 27 tagging was only 1.04 inches. The weight, in micrograms per inch, 18 days after secondary thickening began was 4.54 for the July 20 samples and 4.31 for the July 26 to 27 samples. A cold rain fell on July 21 and the temperature did

not rise above 66° F. that day. The temperature rose to 80° for a short time on the 22nd, and the following days were warm, but few squares were set during the next two or three days. It is suggested by these observations that the effects due to the cool weather were responsible for the delay in secondary thickening which was initiated in these fibres on the 19th day after flowering. Flowers from the same plants tagged on July 26 and 27 showed secondary thickening 17 days and those tagged on August 3, 16 days after flowering.

Since the July 20 series produced a longer and heavier fibre, it might be assumed that the weather between this date and July 27 was more favorable to its growth than it was to that of the later series at the same interval of its development. It is quite possible, however, that the relatively small number of bolls set on the days immediately following July 20, due presumably to the cool weather, allowed the bolls which did set on that date to obtain an unusually favorable food supply.

These are given only as suggestions, and further data will be necessary to determine the effects of weather conditions at the time of flowering on the properties of the fibres at later stages of development.

As was stated before, the wax showed preferred orientation in regard to the long axis of the fibre. The most prominent wax ring is located just inside the 002 cellulose ring which corresponds to a 3.98 Å plane spacing. Measurements indicated that it is the 4.14 Å side spacing which Müller and Saville [15] and others have found to be typical of long chain aliphatic hydrocarbons, acids, alcohols, and waxes. Gunderman, Wergin and Hess [8] found this spacing in patterns of young cotton fibres and thereby helped to clarify the literature concerning the "primärsubstanz" discussed by Wergin [20] and Hess, Trogus and Wergin.[9] This indicates that the molecules of the "wax" are aligned with their long axis transverse to the fibre axis, or parallel to the long axis of the cellulose molecules in the primary wall. Sisson [19] observed that certain samples showed preferred orientation of the waxes but, since he did not find preferred orientation of the cellulose in the primary wall, he apparently did not consider the similarity of orientation, nor the possible association of the two substances.

The data presented in this paper, moreover, are of further importance since they support the microscopic observations of Levine,[14] Balls,[3] Anderson and Kerr [2] and Wergin,[21] all of whom found that the cellulose of the primary wall of the cotton fibre is arranged transverse to the long axis of the fibre. In this connection, Kerr and Bailey,[12] and others have found comparable conditions in wood fibres where the cellulose of the cambial or primary wall is arranged transverse to the fibre axis, and Castle [5] reported transverse arrangement of the chitin fibrils in the primary wall of the sporangiophore of Phycomyces.

In spite of the variations in certain fibre properties observed in this study, corresponding changes extending from the primary to the secondary wall structure were observed in the X-ray diffraction patterns of six different series of samples, representing three species of cotton. Development was relatively rapid and daily collections did not show all stages of the transition except in the series of Mexican Big Boll cotton tagged on July 20. More frequent collections would, no doubt, have shown the same transition stages in all of the series studied.

The results of this X-ray study with regard to the orientation of cellulose in the primary wall disagree in certain respects with the observation of

Sisson.[10] He reported random orientation of the cellulose in the fibres he studied until about the 25th day after flowering, at which time preferred orientation in the direction of the fibre axis became evident. The preferred orientation observed by him was due apparently to the presence of secondary thickening, whereas the random orientation may be attributed to the primary wall or a combination of the two during the early stages of secondary thickening. It is believed that Sisson's failure to observe preferred orientation in the primary wall was due to the technique he described as that used in preparing his specimens.

It is very difficult to prepare representative samples of young cotton fibre. When they are removed from the boll they are sticky and unite into a horny mass upon drying. Washing them in cold water has very little effect, but boiling water gelatinizes the surfaces and reduces the friction between fibres and tends to straighten them out so that they can be paralleled with little difficulty. When secondary thickening is initiated, the gelatinous surface appears to become more plastic, thus increasing the drag between fibres and boiling water has less effect on them. If the fibres during these early stages are first treated with alcohol or other preservative reagents, the surface layer is irreversibly set and does not respond to the boiling water treatment. Similarly the fibres stick together upon drying, and to date no chemical reagent is known by the writer that will separate them without breaking down the fibre structure.

Sisson [10] states that he prepared a part of his specimens "—by carefully dissecting from the seed a few fibres which were first arranged parallel, and then transferred to a glass plate. . . . A number of small bundles of parallel fibres were thus built up and allowed to dry. The final larger bundle consisted of several smaller bundles wrapped together—." The balance of his samples were prepared as follows: "Earlier than 15 days, parallel bundles smaller than those described above were built up by placing fibres over the open end of a glass tube. Upon drying, the fibre ends adhered to the glass, producing in the bundle a tension which helped to parallel the fibres. A similar technique was employed in preparing some of the samples later discussed under the heading of induced orientation." He does not mention boiling the fibres in water before attempting to parallel them, and from his description it seems as if appreciable tension was developed on the fibres during drying; if so, this could have distorted the natural structure.

In another experiment Sisson [17] had previously stated that, "If a large section of the membrane is allowed to dry with the flat surface resting on a horizontal glass plate, the dried sheet peeled off and subjected to X-ray analysis, a selective uniplanar orientation is found—"; or if, "A rod-like strip of swollen membrane was stretched across the end of a beaker, the ends taped to the sides of the beaker, and the strip allowed to dry. The shrinkage accompanying drying caused the strip to become very taut. X-ray diagrams show a uniaxial orientation—." From this, therefore, it would appear that if these methods were effective in inducing orientation in one case, they should also be expected to do likewise in another.

An attempt has been made by the writer to prepare bundles of fibres by spreading thin films of them on glass plates and by stretching them over the open end of a glass cylinder. It was found that, if the layers of fibres on the glass plate were very thin, the X-ray patterns showed less pronounced preferred orientation than when prepared by the methods described in this

paper. However, random arrangement was not observed in any case. It was difficult to remove the thin layers of fibres from the glass plate and to arrange them in bundles such that the fibres were all parallel. They were frail and would not permit the pressure necessary to tie or wrap the bundles in the usual way. Similar patterns were obtained from a bundle which was stretched over the end of a tube to dry. In the latter case the bundle broke while drying due to the tension resulting from shrinkage. In one bundle, which was dried on a glass plate, the pattern showed a very pronounced transverse arrangement, even more so than when prepared in the usual way. It should be pointed out, however, that the fibres in this case were not spread in thin films but that all fibres from a number of seeds were first paralleled and then stretched on the plate together as a bundle. A very small percentage of the fibre contacted the glass, therefore, and the bundle could shrink fully on drying. Thus, in making interpretations and drawing conclusions from X-ray patterns, too much importance can hardly be given to the technique employed in selecting and preparing the original samples or bundles of fibres.

These results seem to indicate that there are two possible reasons why Sisson failed to show transverse arrangement of the cellulose in the primary wall: First, he probably did not completely parallel the fibres; and second, he apparently treated them in such a way as to distort the structure, thus making it impossible to determine what the original arrangement of the cellulose actually was.

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Electrophoretic Studies of Silk

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A Textile Foundation Publication

Abstract

A micro-electrophoretic technique was used to determine the characteristic pH-mobility curves for fibroin and for sericin and to ascertain the extent of removal of the latter during degumming by the soap and enzyme processes. The data suggest that sericin contains a much greater proportion of reactive groups than fibroin, and indicate the importance of obtaining either uniform or complete removal of sericin during degumming processes.

The isoelectric points are shown to vary slightly with ionic strength. In acetate buffers of 0.02 M ionic strength, the isoelectric point of fibroin is 3.6 and that of sericin, 4.3.

Large ions of complex structure such as phthalate or picrate appear to have specific effects which are readily detectable by the electrophoretic technique.

Dissolved fibroin adsorbed on glass particles and fibroin regenerated from similar solutions had the same isoelectric points but different pH-mobility curves. Fibroin regenerated after dissolving in solutions of lithium bromide gave the same pH-mobility curve as untreated fibroin.

Introduction

ONE of the principal difficulties involved in defining many of the characteristics of silk results from the fact that the naturally-occurring fibre consists of at least two proteins, namely, silk fibroin and silk sericin, which have very different properties. Since the latter is generally removed from the fibre by empirical methods, the available data on many of the properties of the fibroin may be of questionable validity, especially since ordinary chemical methods are inadequate for determining the extent of removal of the sericin.

Sericin is a soluble protein which appears to form a coating on the surface of the fibroin. It has been shown by Abramson and others that a number of surfaces, when coated with any one of several proteins, assume electrophoretic properties similar to those of the adsorbed materials, and it was felt therefore, that an electrophoretic technique could be employed to advantage in studies of silk. Such an approach can not only be used for studying the removal of sericin from fibroin but also has the additional

* Research Associates for the Textile Foundation at the National Bureau of Standards. This is the second publication of the new research program of the Textile Foundation at the National Bureau of Standards.

advantage of contributing information relative to the amphoteric properties of the constituents of the naturally-occurring fibre.

Electrophoretic techniques have been frequently used to investigate the properties of protein surfaces. Excellent discussions and reviews on the general subject have been presented by Abramson,[1, 2] and by Moyer.[3]

One characteristic constant of a protein which is determined by its electrokinetic behavior is the isoelectric point. As defined by Abramson,[1] the isoelectric state of a surface of a particle is that electrical state in which the sum of the positive and negative charges at the surface over a time average is equal to zero. The isoelectric point then is defined as the reference concentration of hydrogen ion or some other ion (Th^{++++}, for example) at which this condition is found. In other words, although it has become customary to define the isoelectric point in terms of the pH scale, it must be defined in terms which include a complete description of the medium in which no migration takes place. In the electrophoretic technique, the isoelectric point is, therefore, the point at which the electric mobility is zero.

It has been assumed by some investigators that the isoelectric state of a substance depends only on the state of its dissociable acid and basic groups (its combination with hydrogen or hydroxyl ions). Actually, however, it depends not only on the combination with hydrogen or hydroxyl ions but also with other anions or cations which may be in the solution.* The point at which dissociable groups of the substance combine equally and only with hydrogen and hydroxyl ions is defined as the *isoionic point*.[4] It should be noted that this is identical with the isoelectric point only when the substance does not combine with ions other than hydrogen or hydroxyl. It follows then, that while it may be possible to determine the isoelectric point by several methods, (*e.g.*, by titration provided the substance binds *only* H^+ or OH^-), electrophoresis is the only method by which the isoelectric point is determined in every case.

The most satisfactory results with electrophoretic techniques have been obtained with soluble proteins in solution or adsorbed on inert surfaces such as quartz, glass, or paraffin oil. In many cases it has been found that a protein adsorbed on such a surface has electrokinetic properties which are very similar to those obtained for the same protein when studied in the dissolved state or in the form of relatively insoluble particles. It has also been noted by Abramson that the titration and mobility curves are congruent for a number of soluble proteins, and by making certain assumptions, he has predicted the following: in solutions of the same ionic strength, the electric mobility of the same protein at different hydrogen ion activities should be directed proportional to the number of hydrogen or hydroxyl ions bound by each molecule. In the case of some of the soluble proteins, the isoelectric and isoionic points have been found to be approximately the same.

Considerably more difficulty, however, is encountered in interpreting the results of investigations dealing with insoluble materials, especially those which are more or less crystalline in nature.[6] For example, in some materials of this type, the isoelectric and isoionic points have been found to be far apart. As a result, no attempt is made, at this time, to relate the data obtained to the specific acidic and basic properties of silk. However, it was found that the electrophoretic technique provided an excellent tool for distinguishing protein surfaces and it was in this connection that it was used in the present investigation.

* It should be noted that a surface may conceivably adsorb hydrogen or hydroxyl ions other than those bound by the acidic and basic groups.

Description of Apparatus, Methods, and Materials

An Abramson horizontal micro-electrophoresis cell was employed in this investigation. The apparatus and methods were essentially the same as those described by Moyer.[6] The apparatus was checked from time to time by measuring the mobility of human erythrocytes in $M/15$ phosphate buffer at pH 7.4.[7] A 28 × ocular and 40 × water-immersion objective were used for measurements involving soluble proteins adsorbed on glass particles. Particles of ground silk were observed with a 20 × ocular and 20 × objective.

In most cases, the mobilities were measured by observing the velocity during migration of the particles at the 0.21 and 0.79 depth levels of the cell, where the effect of the electroosmotic flow of the liquid is eliminated.[6] When the mobilities were very low, the velocities of the particles were measured in successive layers from the top to the bottom of the cell, and the mobility was evaluated by graphical integration of the curve obtained by plotting velocity against depth.[1]

The majority of measurements were made on samples of raw and degummed silk which were reduced to a suitable particle size by cutting in a small laboratory Wiley mill until the particles passed through a 60-mesh screen. A suspension of the particles in water was made and allowed to settle. The supernatant liquid was removed and found to contain particles approximately 1 to 5 microns in diameter.

The mobilities of dissolved silk or sericin were measured by adsorption of the protein on particles of Pyrex glass of 0.1 to 2 microns diameter. The particles were thoroughly cleaned by washing with cleaning solution, water, concentrated hydrochloric acid, water, 0.001 N ammonium hydroxide, and then finally soaked for three days in distilled water, during which time the water was changed daily.

The mobilities of soluble materials were always measured in solutions containing a concentration of protein sufficient to insure complete coating of the glass particles. The required concentration was determined by measuring the mobility as a function of concentration of protein at constant pH, and determining the point beyond which further increase in protein concentration caused no further change in the mobility of the glass particles.

All mobility measurements were made in a room at approximately 25° C. All values were corrected to 25° C. by applying a factor of 2% per degree.[6]

pH values of the suspensions were measured with a MacInnes and Belcher type glass electrode and an electron ray meter. The pH values were referred to potassium acid phthalate (0.05 M) which was assigned a pH value of 4.01.[8]

The silk used was the product of the silkworm "*Bombyx mori.*"

Experimental

Electrophoretic Properties of Raw Silk.

Curve 1 in Fig. 1 shows the mobilities as a function of pH for three different samples of raw silk. The mobilities were measured after overnight immersion of the particles in hydrochloric acid—potassium chloride (pH range of 1.7 to 3.0) or acetic acid—sodium acedate (pH range of 3.0

to 6.5) solutions of ionic strength 0.02. Since sericin is relatively soluble it was expected that some of the material would dissolve in this time and then completely coat the particles of cut up silk. That curve 1 actually

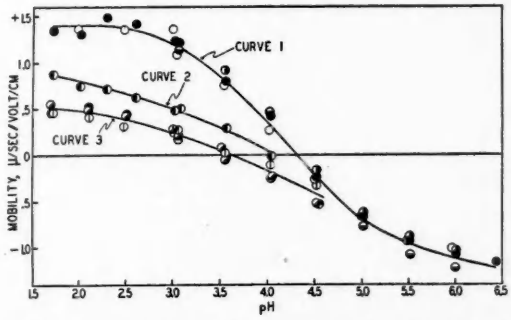

FIG. 1. A comparison of the pH-mobility curves for raw and degummed silks. Curve 1 represents the mobilities for 3 different samples of raw silk, ●, ◒, ◑, and for sericin adsorbed on glass particles, ○. Curve 2 is that for silk degummed for 2 hours with soap. Curve 3 represents the results for 1, 2, and 3 cycles of degumming treatment as listed in the text.

represents the mobility of sericin adsorbed on silk was demonstrated by the following experiments.

A sample of sericin was obtained by boiling 10 g. of natural silk in two 150 ml. portions of water for 15 minutes each. One drop of a suspension of Pyrex particles was then added to each of a series of solutions of

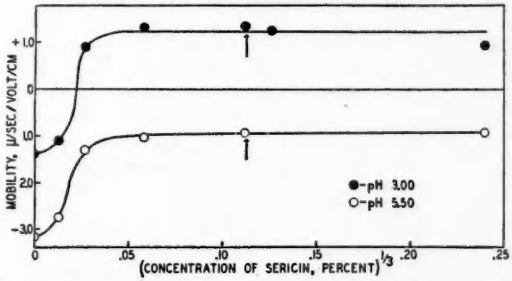

FIG. 2. Mobility as a function of concentration of sericin at pH 3.0 and pH 5.5, in 0.02 *M* ionic strength buffers.

the same pH but containing varying amounts of sericin. The mobilities of the glass particles were measured after allowing 15 minutes for adsorption. The two curves, shown in Fig. 2, were obtained by plotting mobility as a function of sericin concentration and indicate that complete coating of the glass particles by sericin occurs in solutions containing as

little as 0.0001% of sericin. The mobility of sericin adsorbed on glass was then measured as a function of pH. The solutions used contained approximately 0.001% of the protein. The results as shown by the open circles in curve 1, Fig. 1, indicate that the pH-mobility curve for the adsorbed sericin is identical with that obtained for the sericin on the silk fibres. The data also indicate that the sericin is isoelectric at pH 4.3.

Electrophoretic Properties of Degummed Silk.

Soap Degumming. 50 g. of natural silk was boiled successively in four 2-liter portions of a 1% solution of soap for a total time of 2 hours, then extracted with cold alcohol and ether and finally washed twice with water at 50° C. Curve 2, Fig. 1, is the pH-mobility curve for the degummed sample. After the above degumming treatment, some of the fibres were shaken with a hydrochloric acid-potassium chloride solution (ionic strength 0.02) of pH 1.77 containing some glass particles. It was found that an amount of sericin sufficient to alter the mobility of the glass particles was still present.

In an attempt to remove all of the sericin from the fibres, 10 g. samples of the silk were subjected to successive cycles of the following treatments: a boil-off in 2-liter portions of a 1% solution of soap for 3 successive ½ hour periods, a 5-minute boil in 2 liters of water, a 5-minute rinse in 2 liters of 0.1 *N* ammonium hydroxide, a 5-minute rinse in 2 liters of 0.1 *N* hydrochloric acid, a 1-day wash in running distilled water, a 4-hour extraction with cold alcohol, and finally 3 successive rinses in distilled water at 50° C.

Curve 3, Fig. 1, shows results for samples subjected to one, two, and three cycles of the above series of treatments. No measurable change was produced after the first treatment, which appears to indicate that the samples were completely degummed. Curve 3 therefore represents the pH-mobility curve for fibroin, and indicates that the material is isoelectric at pH 3.6 in 0.02 ionic strength acetate buffers.

Enzyme Degumming. A 10-g. sample of silk was treated with 1 liter of a solution containing 20 ml. of serizyme (papain) at 50° C. for a total of about 500 hours. The enzyme solution was changed three times during the first 100 hours of treatment. Removal of sericin as measured by loss in weight and nitrogen determinations was rapid during the first 50 hours of treatment. The fibres continued to lose weight during the first 400 hours but appeared to reach a constant value after that time.

Fig. 3 shows the results of pH-mobility measurements on the sample in hydrochloric acid—potassium chloride and acetic acid—sodium acetate solutions (ionic strength 0.005).*

Similar measurements, made at the same ionic strength on a sample which had been completely degummed by the soap boil-off method, are included in the figure. The data obtained on the two samples are in good agreement and indicate the complete removal of the sericin.

Effect of Variation of Ionic Strength.

The curves in Fig. 4 represent data for soap-degummed fibroin in hydrochloric acid—potassium chloride buffers of 0.005, 0.02, and 0.05 ionic strength. The maximum shift in isoelectric point in these solutions is approximately 0.4 pH unit.

* The ionic strength was decreased from 0.02 used previously to 0.005 in order to facilitate measurements by increasing the mobilities.

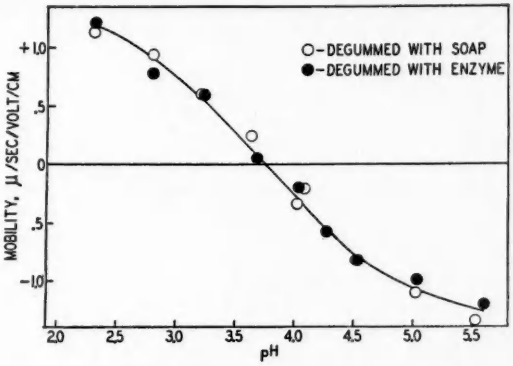

FIG. 3. A comparison of pH-mobility curves for silk degummed by soap and enzyme treatments.

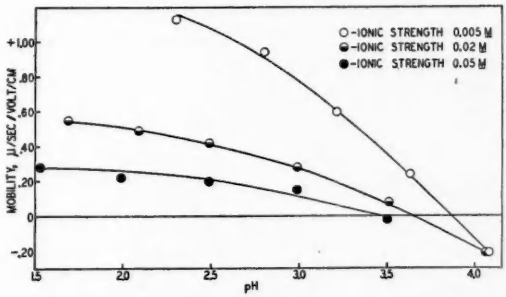

FIG. 4. Effect of variation of ionic strength on the pH-mobility curve of degummed silk.

Fig. 5 represents similar curves at 0.005 and 0.02 ionic strength for dissolved fibroin coated on glass particles. The material was prepared as follows: 0.5 g. of degummed fibroin was heated in 5 ml. of a 50% solution of lithium bromide (specific gravity 1.53) on the steam bath for 5 minutes. The solution was dialyzed (specific resistance approximately 30,000 ohms), coated on glass particles, and the mobilities were measured. The curves show that the same relation between mobility and ionic strength holds for the dissolved fibroin as for the solid material.

Specific Ion Effects.

The isoelectric points (3.5–3.9) obtained in the present investigation are higher than that (2.5) previously reported by Harris.[9] The differences appear to be too large to be accounted for by the differences in ionic strengths used in the two investigations. However, it was noted that

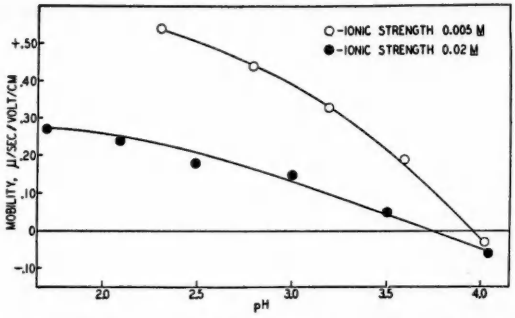

FIG. 5. Effect of variation of ionic strength on the pH-mobility curve of dissolved fibroin adsorbed on glass particles.

hydrochloric acid—potassium acid phthalate buffers were used in the earlier investigations, which suggested that the differences might result from specific ion effects.

The effect of different ions in shifting the point of maximum flocculation and other protein characteristics has long been recognized.[10,11] This is especially true for polyvalent ions.[12] Fig. 6 shows results of pH-mobility measurements in six different types of solutions on fibroin degummed

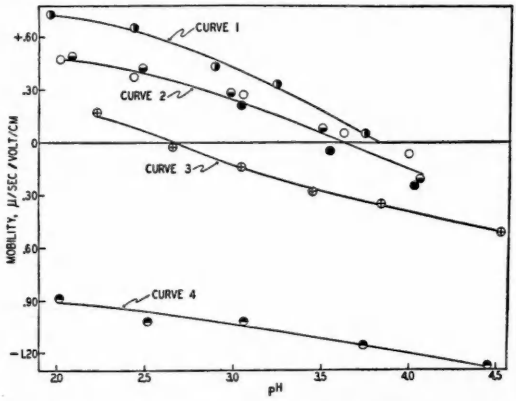

FIG. 6. Effect of different ions on the electrophoretic mobility of degummed silk. Curve 1, oxalic acid-potassium hydroxide solutions. Curve 2, solutions of hydrochloric acid-potassium hydroxide, ◒; sulfuric acid-potassium hydroxide, ○; and acetic acid-sodium hydroxide, ●. Curve 3, Clark's phthalate buffers. Curve 4, picric acid-potassium hydroxide solutions.

by the soap boil-off method. All of the buffers except the phthalate were of ionic strength 0.02. The phthalate solutions varied in ionic strength from 0.05 to 0.10.

Curve 2 represents the data obtained in the hydrochloric acid—potassium chloride, acetic acid—sodium acetate, and sulfuric acid—potassium sulfate solutions. In these systems, the samples were isoelectric at about pH 3.6, although there may have been slight divergences between the different valence types. The phthalate buffers (curve 3) caused a shift in the isoelectric point of approximately 1 pH unit to pH 2.6, in agreement with the data of Harris.* Oxalic acid causes a smaller shift in the opposite direction (curve 1). In the picrate solutions (curve 4), the sample was so electro-negative that it no longer exhibited an isoelectric point in the pH range used.

Effect of State of Aggregation.

Silk is readily dissolved by concentrated solutions of certain neutral salts.[13, 14, 15] With some salts, such as lithium bromide, solution is accomplished at room temperature.

A sample of degummed silk was dissolved by shaking with a 50% solution of lithium bromide at room temperature for several hours and the solution dialyzed against running distilled water. After about 2 days a precipitate was formed. Microscopic examination of the material showed it to be made up of well-defined fibres which were strongly birefringent.

When the fibroin was dissolved by heating in a lithium bromide solution on a steam bath, spontaneous formation of a fibrous material did not occur during subsequent dialysis. On addition of ether, a precipitate which appeared to be somewhat fibrous and of low-order birefringence was obtained.

pH-mobility curves in solutions of 0.005 *M* ionic strength for both samples of regenerated fibroin as well as for the dissolved materials coated on glass particles are given in Fig. 7.

Discussion

A comparison of the curve for sericin (curve 1, Fig. 1) with that for fibroin (curve 3, Fig. 1) shows that the mobility of the former is much greater, which strongly suggests that sericin contains a much greater proportion of the reactive carboxyl and basic amino groups. This has recently been confirmed by chemical analyses.[16] The practical significance is at once obvious. Many of the problems related to silk and silk processing are in part, at least, concerned with the surface characteristics of the fibre. For example, the presence of a small amount of sericin may have a profound influence on the dyeing properties, and uneven distribution of the residual sericin would probably result in uneven dyeing of the fibres. It is not within the scope of the present investigation, however, to do more than point out some of the implications of these electrophoretic studies. The relationship of the difference in chemical properties between fibroin and

* The results for phthalate solutions (Clark's buffers) are not directly comparable with those for the other buffer types because of the difference in ionic strengths. However, the data given above for fibroin in solutions of different ionic strengths indicate that only a minor portion of the shift is caused by this factor. This is confirmed by the fact that a fivefold decrease in the ionic strengths of Clark's buffers causes an increase of only about 0.3 pH unit in the isoelectric point of wool.[16]

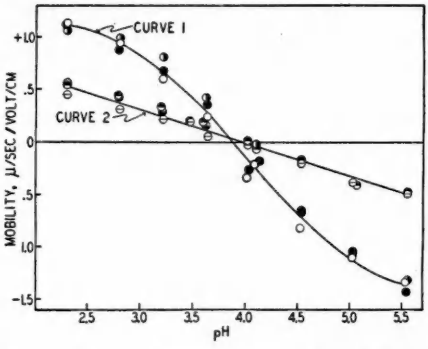

FIG. 7. Effect of state of aggregation on the electrophoretic mobility of fibroin. Curve 1 represents the mobilities of degummed fibroin, ○. fibroin regenerated after solution in hot lithium bromide; ◑; and fibroin regenerated after solution in lithium bromide at room temperature, ●; Curve 2 is for dissolved fibroin adsorbed on glass. The solutions were obtained by heating fibroin in solutions of lithium bromide for 5 minutes, ◓, and for 2 hours, ◒, and by solution of fibroin at room temperature, ⊖.

sericin to the more practical aspects of silk chemistry is being studied separately.[16]

The specific ion effects noted in Fig. 4 indicate that considerable care must be exercised in choosing buffer systems for protein investigations. These data also emphasize the necessity of including in the definition of the isoelectric point a description of the medium in which no migration takes place.

Sufficient data are not available for the elucidation of the nature of specific ion effects. In general, it appears that the greatest anomalies arise when large ions of complex structure such as phthalate or picrate are used. The results suggest a number of possible explanations. For example, the acid of the buffer solution might react with basic groups of the fibroin to form a slightly ionized compound; the anion might react with, or be adsorbed by the fibre in such a manner as to allow one of the acid groups of the adsorbed ion to be free; the strength of the acid or basic groups in the fibre might be altered by the proximity of the polar groups of the anion; or the adsorbed anion might provide charged centers which might even permit the adsorption of other ions.

It is well known that picric acid forms compounds with many proteins. Silk undoubtedly also forms picrates as evidenced by the color of the fibres. In the case of colorless ions such as phthalate ions, however, similar reactions are not at once obvious. The electrophoretic technique accordingly may often prove useful as a qualitative indication of such reactions.

Examination of the curves in Fig. 7 reveals a number of points of interest. The dissolved fibroin, adsorped on glass particles (curve 2) exhibits lower mobilities than the untreated or regenerated fibroin (curve

1) throughout the pH range tested. The mobilities of the undissolved fibroin were roughly twice those of the dissolved material adsorbed either on glass or quartz particles. These data are in disagreement with earlier data by Harris[9] in which it appeared that the mobilities were the same. The present work, however, indicates that the solutions used previously were too concentrated and, as a result, the majority of particles appearing in the solution were those of regenerated fibroin. These, as shown (solid and half-solid circles, curve 1), give a pH-mobility curve which is identical with that of untreated fibroin (open circles, curve 1).

Although only one curve is drawn to represent the points for the solid fibroin and one for the points for the dissolved material, it appears that dissolving fibroin in hot solutions may have produced slight alterations in it. For example, in curve 2 the points for the material obtained by solution at room temperature are consistently below those obtained for material dissolved in the hot solutions. The differences, however, are too small to warrant any further conclusions at this time.

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16. Publication in preparation.

Abstracts

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I. Fibres (Synthetic and Natural) and Fibre Analysis

German Fibre Plants: Cultivation. Ulbricht. *Klepzig's Textil-Z.*, 1938, V. 41, P. 697–99, 708–10, 719; abs. in *J. T. I.*, March 1939, P. A147.

A survey is made of the conditions of cultivation and methods of fibre extraction and the possible yields, value and uses of various plants growing in Germany that could be used as sources of textile fibres. These include flax, hemp, nettles, hops, broom, mallow, willow, ramie, yucca, etc. Fibres from mulberry stems, pine wool, wool grass, and seed hairs of the thistle, silk plant, reed-mace, etc., are also mentioned. (C)

Italian Textile Fibres: Production. G. Blumenthal. *Chimie et Ind.*, 1938, V. 40, P. 1248–51; abs. in *J. T. I.*, March 1939, P. A147.

Italy now leads among European countries for artificial textiles, producing 16% of the world's output and exporting 30% of the world's total exports. Further increase in artificial fibres is expected by the use of native Ethiopian plants. An account, with figures, is given of the Italian production of hemp, linen, cotton, broom, mulberry bark, ramie, rayon, Lanital, wool and silk. (C)

Karakul: Investigations on Downy Hair and Lock Formation in the. L. Adametz. *Z. f. Züchtung, B*, 1938, V. 41, P. 90–106; abs. in *J. T. I.*, Feb. 1939, P. A81.

The various forms of locks in different types of Karakuls are analyzed. The conclusion is reached that in both the "Flaumhaar" (downy hair) and

the "Grannenhaar" (long, coarse hair) no one single characteristic is responsible for the formation of the varying locks. (C)

LANITAL FIBRE: FORMALDEHYDE CONTENT AND STRENGTH. H. Rath and A. Essig. *Klepzig's Textil-Z.*, 1938, V. 41, P. 463–66; abs. in *J. T. I.*, Dec. 1938, P. A761.

The function of formaldehyde in Lanital is discussed and a method for the quantitative determination of the formaldehyde content is described which depends on boiling the fibre in dilute sulphuric acid and colorimetric determination of the formaldehyde content of the solution with fuchsine sulphurous acid. Results obtained for various Lanital products are given. (C)

NITROCELLULOSE: INFLUENCE OF PRE-TREATMENT OF COTTON ON QUALITY OF. A. Bresser. *Brit. Plastics*, July 1938, V. 10, P. 60–1; abs. in *Eastman Kodak Abs. Bull.*, Dec. 1938, P. 592.

The processes of soda-boiling and bleaching of cotton linters can be so controlled that the behavior of the cotton on nitration can be guaranteed. (S)

REGENERATED CELLULOSE FILAMENTS: MICELLAR STRUCTURE AND DEFORMATION. P. H. Hermans. *Leipz. Monats. Text. Ind.*, 1938, V. 53, P. 305–8; abs. in *J. T. I.*, Mar. 1939, P. A187.

The micellar structure of regenerated cellulose filaments and the results of X-ray studies and investigations of the anisotropy of swelling are discussed and it is shown how swelling, elasticity and strength effects can be explained by the assumption of a network structure built up from micelles having fringe-like ends. (C)

SILKWORM FIBROINOGEN: COAGULATION. W. Ramsden. *Nature*, 1938, V. 142, P. 1120; abs. in *J. T. I.*, Feb. 1939, P. A81.

In seeking to learn how the silkworm converts the stiff water-soluble fibroinogen paste into insoluble fibroin the author has effected the conversion by shearing the paste between flat plates, or by freezing at — 13 to — 17° C. The latter may be due to a shearing effect of ice crystals and the author suggests that the conversion by the silkworm may be due entirely to shearing in the silk-channels. (C)

II. YARNS AND FABRICS

RAYON CRÊPE YARN: CHARACTERISTICS. *Rusta*, 1938, V. 13, P. 320–23, 446–7; abs. in *J. T. I.*, Nov. 1938, P. A657; Feb. 1939, P. A125.

The characteristics of a 48-filament viscose rayon yarn of 100 denier before and after crêpe twisting are discussed, and a theoretical and graphical study is made of the work done in twisting, the energy accumulated in the crêpe yarn, the tension, the untwisting force, and the extension at break. (C)

RAYON FABRIC: DEFECTS DUE TO IRREGULAR YARN SHRINKAGE. K. Langer. *Kunstseide*, 1938, V. 20, P. 425–28; abs. in *J. T. I.*, March 1939, P. A190.

It is pointed out that rayon which has been stretched beyond its elastic limit shrinks on wetting and that such shrinkage may give rise to faults in

finished fabrics. The examination of a warp knitted charmeuse fabric showing light and dark stripes which were found to be due to irregular shrinkage is described. Yarns from the portions giving the light and dark stripes showed differences in extensibility before but not after the dyeing operation. Tests of samples of the original yarn supply showed a much greater shrinkage in water than in the case of samples of similar rayon yarn from other sources and also considerable differences between the outer and inner layers on the same bobbin. Apparently the yarn had been wound with a constant spindle speed with the result that stretching of the yarn increased with increasing diameter of the bobbin. The differences in shrinkage on dyeing produced differences in stitch size and density. (C)

RAYON WARP SLASHING: FUNDAMENTALS OF. W. L. Bentley. *Rayon Tex. Mo.*, 1939, Jan., P. 63–4, 75; Feb., P. 61–3; Mar., P. 67–9.

Paper delivered before A. A. T. T., Dec. 7, 1938. (C)

RAYON WARPS: SIZING. W. Schramek. *Leipz. Monats. Text. Ind.*, 1938, V. 53, P. 275–79; abs. in *J. T. I.*, Jan. 1939, P. A22.

Developments in the sizing of rayon yarns are discussed and it is pointed out that tests based on measurements of warp breaks in weaving have shown that in order to obtain sizing effects with polyvinyl and protein sizes equivalent to those obtained with linseed oil in the hank sizing process it is necessary to use relatively high concentrations of the polyvinyl and protein sizes, especially of the latter. In the sizing of rayon warp beams, however, it is possible to obtain better results with these sizes than with linseed oil and the concentrations required are lower than those required in hank sizing. Factors that may be of importance in sizing, such as the adhesive power of the size film, the concentration of the sizing solution, the smoothness of the sized yarns, etc., are outlined and the results of adhesive power and smoothness tests on polyvinyl alcohol and protein sizes and various proprietary products (Tylose, Blufajo, V. R., etc.) are given. It is shown that in many cases an indication of the value of a sizing preparation can be obtained from a study of the adhesive power of the size film and the smoothness of the sized yarn, a size with a low adhesive power often being effective if it gives high smoothness and vice verse. (C)

RAYON AND STAPLE FIBRE CRÊPE FABRICS. A. Jaumann. *Kunstseide*, 1938, V. 20, P. 389–98; abs. in *J. T. I.*, Feb. 1939, P. A101.

The use of rayon and staple fibre for the production of crêpes, the different types of crêpe effects obtainable, the requirements of a rayon crêpe yarn, and the suitability of rayons and staple fibres of different type and fineness for the production of different effects are discussed. It is pointed out that in the case of rayon crêpes, the shrinkage in the crêpe finishing process, and consequently the crêpe effect produced, depends not only on the yarn twist but also on over-extension and swelling of the rayon and that less twist is required in rayon crêpe yarns than in cotton crêpe yarns of corresponding counts. Crêpe fabrics can be produced without a crêpeing treatment by the use of spiral and bouclé yarns. Such fabrics generally show satisfactory resistance to creasing and, provided the core threads are not highly twisted, shrink little on wetting. (C)

STAPLE FIBRE FABRICS: THERMAL INSULATING POWER. A. Zart. *Monatsh. Seide u. Kunstseide*, 1938, V. 43, P. 324–27; abs. in *J. T. I.*, Dec. 1938, P. A765. (C)

SIZING SPUN RAYON: HOW STARCHES ARE USED IN. J. F. Fitzgerald. *Rayon Warp Sizing Specialist*, Jan. 1939. (C)

WOOLEN CARDING PRINCIPLES AND REFINEMENTS. P. P. Townend. *Text. Mfr.*, Mar. 1939, P. 104–5.

Some recent ideas in principles of woolen carding as they affect the construction and recent refinements in woolen cards. (C)

WOOL: NEW PROBLEMS IN THE FINISHING OF. E. Elöd and H. Rudolph. *Mell. Textilber.*, 1939, No. 3, P. 211.

Systematic research into the properties of the wool proteins and into the processes that take place during the familiar finishing processes has given rise to a large number of problems connected with the aim of adapting the finishing processes of wool better than has hitherto been done to the peculiarities of the proteins of wool, in order to preserve to the maximum extent the valuable physical, mechanical, and chemical properties of the wool fibre. The proteins of wool, as is well known, are more sensitive to the action of alkalis than of acids, even when the distance from the isoelectric point is the same in each case. The investigators have published a number of articles dealing with the problem of the "slight injury to wool," that is to say, with injury that cannot be definitely disclosed by means of the ordinary mechanical testing methods. It has repeatedly been pointed out that most of the familiar color reactions for the discovery of injury to wool have only a limited value and may lead to wrong conclusions, because they are carried out without regard to the condition of the wool in respect of its pH condition. The extensive series of tests carried out in this sense, for example, carbonizing wool under various conditions, or on the effect of acids and alkalis, and finally on the process of scouring raw wool, have disclosed a number of valuable points of view. Details of further experiments are not given in the present article and the investigators confine themselves to tabulating the results in a diagram, from which it can be seen that the method of scouring wool with due regard to its isoelectric point plainly tends to preserve the properties of the fibres. The investigations show that it is possible, not only in the laboratory, but especially also on a manufacturing scale, to effect fundamental changes in the methods of scouring wool on the lines indicated, whereby a really high-class fibre is finally produced when the various finishing processes that follow (drying, dyeing, carbonizing, decatizing, and so on) are also carried out with due regard to the various points of view that have repeatedly been explained by the authors. (C)

WORSTED HAIR YARNS: BLENDING WITH WOOL. "Distaff." *Canadian Text. J.*, 1938, V. 55, No. 17, P. 33–4; abs. in *J. T. I.*, Nov. 1938, P. A656.

The blending of alpaca, mohair and other smooth fibres with wool to obtain special yarn effects is described. Tables are given showing (1) suggested blends, and (2) the properties of vicuna, cashmere, alpaca, camel hair, mohair and llama as compared with fine wool. (C)

YARN: PROGRESS IN CURLING OF. Thos. Broadbent & Sons, Ltd. *Text. Mfr.*, Mar. 1939, P. 95–7.

Summary of a booklet of Thomas Broadbent & Sons, Ltd., Huddersfield, Eng., describing and illustrating the curling of animal fibres and the machines employed. (C)

YARN TWIST: THEORIES. *Revue Textile*, 1938, V. 36, P. 539–49; abs. in *J. T. I.*, March 1939, P. A188.

Two theories of twist, proposed respectively by Gegauff and Müller, are explained. The first maintains that twist does not fatigue the fibres and that elasticity increases with twist, the other affirms that, beyond a certain limit, increasing twist fatigues the fibres and even causes them to break, and that elasticity diminishes with increasing twist since it is a minimum in fine yarns at the critical twist. Each author claims that practical results are in agreement with his theory. (C)

III. CHEMICAL AND OTHER PROCESSING (NOT OTHERWISE CLASSIFIED)

CELLULOSE ACETATE: SWELLING AND DYEING. J. Rolland. *17me Congrès Chim. Ind.*, 1937, P. 182–89; abs. in *J. T. I.*, Jan. 1939, P. A33.

A general discussion is given of the phenomena of swelling in cellulose acetate, due to which the rather hydrophobic material can be delustred and relustred, dyed, printed and weighted. (C)

CELLULOSE ACETATE RAYON: DYEING. *Teintex*, 1938, V. 3, P. 527–35; abs. in *J. T. I.*, Jan. 1939, P. A33.

Methods of dyeing cellulose acetate rayon, including numerous patent processes, are classified into (a) methods depending on superficial saponification followed by dyeing with direct and basic dyes, (b) procedures based on swelling the fibre and dyeing with the usual cotton and wool dyes, (c) methods involving the use of special soluble dyes, such as Ionamines, Duranols, etc., and (d) methods depending on the use of dispersed dyes, such as SRA Dispersol and Celatene dyes, and are reviewed. (C)

CELLULOSE ACETATE FABRICS: PATTERNING BY PARTIAL DESTRUCTION. Société Rhodiaseta. *Rusta*, 1938, V. 13, P. 349–53; abs. in *J. T. I.*, Dec. 1938, P. A746.

Reference is made to the production of designs on fabrics containing cellulose, *e.g.*, velvets with regenerated cellulose pile, by printing with pastes containing aluminium chloride and steaming to destroy the regenerated cellulose, and attempts to produce patterns by local destruction of cellulose acetate rayon are critically discussed. Details are given of the method depending on printing with pastes containing benzoyl peroxide. The production of special effects on fabrics composed of three types of fibre is briefly discussed. Notes are given on the nature, storage and use of the products employed in such printing processes. (C)

CELLULOSE ETHER SIZING AND FINISHING AGENTS: APPLICATION. K. Sponsel. *Mell. Textilber.*, 1938, V. 19, P. 738–39.

The disadvantages of the finishes produced with the usual finishing agents such as starch, especially their lack of resistance to washing and wear, are pointed out and the use of non-thermoplastic cellulose derivatives and various polymerized products is discussed. The characteristics required of these materials are explained and various commercial cellulose ether products are mentioned. For the finishing of cotton, rayon and staple fibre fabrics, alkali-soluble products such as Tylose 4S, Ceglin and Cellophas, which swell but do not dissolve in water, are used. Procedures for

the production of permanent finishes are outlined. The alkali-soluble ethers may also be used as sizes for cotton and staple fibre yarns. Water-soluble cellulose ethers, such as Tylose TWA, Thomelose O and S, Cellophas WLD, and Hortol A and S may also be used for sizing and finishing purposes and certain of them have emulsifying and dispersing powers. (C)

COTTON: MERCERIZATION; INFLUENCE OF TEMPERATURE AND ALKALI CONCENTRATION. W. Schramek and H. Thomas. *Leipz. Monats. Text. Ind.*, 1938, V. 53, P. 157–64, 187–94, 219–26, 245–51; abs. in *J. T. I.*, Jan. 1939, P. A32.

The various methods of determining the degree of mercerization of cotton are critically reviewed and classed into (1) methods depending on measurements of changes in the outer form of the fibres, (2) methods depending on measurements of changes in the internal fine structure of the fibres, and (3) methods depending on measurements of changes in chemical and physical properties resulting from the changes in structure. The methods of group (1) serve only for determining whether cotton has been mercerized well, badly or not at all and most of the methods of group (3) are only capable of indicating qualitative differences between mercerized and unmercized material. The only method in group (2) is the X-ray method, and this method and the hydrolysis number method are the only absolute methods for the determination of degree of mercerization, and these can be used for quantitative determinations. Some of the other methods may be used for relative measurements. A detailed account is given of a study of the shrinkage of cotton yarns in caustic soda solution and the results are shown in shrinkage-concentration curves for various temperatures and periods of immersion and in space models showing shrinkage, alkali concentration and temperature. It is concluded that the changes in structure shown in X-ray diagrams can be used as a measure of the technical effect of mercerization, that the changes in structure rather than the shrinkage have the most important influence on lustre, and that strength measurements and dye absorption tests are not suitable bases for the evaluation of technical mercerization effects. The optimum conditions of mercerization, considered from the point of view of shrinkage, change in structure, lustre, and fibre strength, are found at 38–40° C., and alkali concentrations of 20–25% NaOH for a mercerization period of 2½ min. (C)

DEFECTS IN GREY GOODS: FINISHER'S VIEWPOINT ON. C. Norris Rabold. *Cotton*, April 1939, P. 94–6.

Lists some of the common defects in grey goods that cause the finisher difficulty, and shows what is necessary to correct them after they get to the finishing plant, often without success, though at great expense. (C)

DEGUMMING: EFFECT OF—IN FINISHING HOSIERY. Noel D. White. *Cotton*, April 1939, P. 164–68.

Explains why the finishing should start with the degumming and the proper procedure. (C)

IV. RESEARCH METHODS AND APPARATUS

ACID IN WOOL: DETERMINATION OF. *Analyst*, 1938, V. 63, P. 782–97; abs. in *J. T. I.*, Jan. 1939, P. A56. (C)

LANITAL: DETERMINATION IN MIXTURES. G. Baroni. *Boll. Uff. R. Staz. Sper. Seta*, 1938, V. 16, P. 31–40; abs. in *J. T. I.*, March 1939, P. A187.

A new method for the quantitative analysis of material containing wool and Lanital is described, which consists in extraction at 50° C. for 30 min. with 10% (vol.) potassium hydroxide; Lanital suffers a loss of 7.50%. A similar method due to Cerbaro employs 20% caustic soda for 3 hours and the loss of weight suffered by Lanital is 12%. Mixtures of wool, Lanital and cellulose are analyzed, in the absence of acetate rayon, by scouring with soda and dissolving the cellulose in sulphuric acid of 58° Bé., and in the presence of acetate rayon by treatment with benzene and extraction with acetone in a Soxhlet apparatus, followed by the above procedure. Analyses of mixed threads of wool, Lanital, rayon and cotton are made by taking two samples and determining the wool and Lanital in one and the cotton and rayon in the other. Results of various analyses are given. (C)

COTTON FIBRE: STRENGTH TESTING. W. L. Balls. *Rept. 18th Int. Cotton Congress*, 1938, P. 167–72; Discussion, P. 46–9; abs. in *J. T. I.*, Jan. 1939, P. A54.

The author claims advantages for his Impact Tester as a rapid means of determining the strength of cotton fibres. He contends that with Egyptian cottons there is an important "residue" of spinning quality not predictable by hair-weight, length and waste and necessitating a direct measurement of strength. Experience at the Shirley Institute is discussed that suggests that, if maturity is allowed for, the "residue" might be supplied without strength tests. (C)

COTTON FIBRE X-RAY DIAGRAM: ANALYSIS. E. E. Berkley and O. C. Woodyard. *Indus. Eng. Chem., Anal. Ed.*, 1938, V. 10, P. 451–55; abs. in *J. T. I.*, Dec. 1938, P. A760.

For analyzing X-ray diffraction patterns of cotton fibres a microphotometer has been developed, which consists essentially of a constant light source, a simple optical system for limiting the illumination to a very small section of the pattern, a means of measuring the light transmitted by this section with a photo-electric cell and galvanometer system and a method of moving the desired portion of the pattern into the optical path. Bundles of fibre are prepared in the same way as in the Chandler method except for wrapping, details of which are given. The X-ray diffraction patterns are obtained by passing a parallel beam of copper radiation through the bundle held with the long axis perpendicular to the X-ray beam. The diffracted radiation is allowed to fall upon a flat photographic film placed 4 cm. from the centre of the bundle and the prominent and simple arcs resulting from the 002 plane are measured in degrees. (C)

COTTON FIBRES: DETERMINATION OF SWOLLEN DIAMETER OF. EFFECT OF SIZE OF SAMPLE ON SIGNIFICANCE AND RELIABILITY OF RESULTS. R. S. Koshal and N. Ahmad. *J. T. I.*, March 1939, P. T63–T72.

As a result of this investigation, the following procedure for the accurate determination of swollen diameter is recommended: (1) Swollen diameter measurement (as described in this paper) should be carried out by two testers. (2) Each tester should prepare a "maturity slide" and take swollen diameter measurements on 75 fibres for cottons in general and on 100 fibres for special cottons. (3) The mean results obtained by the two test-

ers for the same cotton should not vary by more than 6% for special cottons and 7% for other cottons. If larger differences occur, tests should be repeated by one or both testers. (4) The extreme variation for ($P = 0.05$) which may be expected between two cottons due to random causes is about 5% for mean values based on 150 tests, and about 4% for those based on 200 tests. If larger differences are observed, these may be due to the "specific treatment effects." (C)

COTTON: RAPID METHOD FOR THE ESTIMATION OF REDUCING POWER IN. R. B. Forster, S. M. Kaji, and K. Venkataraman. *J. S. C. I.*, 1938, V. 57, P. 310–15; abs. in *J. Soc. Dyers Col.*, March 1939, P. 170.

Degradation of cellulose is estimated rapidly as follows: The material is extracted with caustic soda solution, acidified, treated with excess ceric sulphate solution, and the excess determined by titration with ferrous ammonium sulphate solution. The process takes less than 1 hr., and no filtrations and transference of cotton or liquor are involved. The conditions of alkali extraction and of ceric sulphate oxidation are so adjusted as to give copper numbers for the reducing power in accordance with Braidy values. For oxycelluloses of Braidy numbers above 2, the new method gives lower values. This divergence of the values from the Braidy copper number in the case of highly degraded oxycelluloses, and the coincidence in the case of highly degraded hydrocelluloses are being examined with regard to the quantitative distinction between oxycellulose and hydrocellulose. (C)

V. PURE SCIENCE, ECONOMICS AND MISC.

RESEARCH: PLACE OF—IN TEXTILE MILLS AND THE TEXTILE INDUSTRY. Carl Schlatter. *Am. Dye. Rptr.*, Oct. 17, 1938, P. 563–67. (C)

SCHARDINGER DEXTRINS: CONSTITUTION. K. Freudenberg and Margot Meyer-Delius. *Ber. Dtsch. chem. Ges.*, 1938, V. 71, P. 1596–1600; abs. in *J. T. I.*, Dec. 1938, P. A779.

Schardinger's α- and β-dextrins were twice methylated by treatment of the sodium derivatives in liquid ammonia with methyl iodide. The properties of the methyldextrins are described. On hydrolysis they both gave 2: 3: 6-trimethylglucose but no trace of di- or tetra-methylglucose. (C)

SPHERO-PROTEINS: STRUCTURE. F. Haurowitz. *Z. physiol. Chem.*, 1938, V. 256, P. 28–32; abs. in *J. T. I.*, March 1939, P. A198.

The author regards as an objection to Wrinch's cyclol theory of protein structure the absence of evidence of the presence of the free hydroxyl groups shown in her formulae. Attempts to methylate oxyhaemoglobin and to acetylate egg albumin are described. (C)

STARCH: ACETYLATION AND MOLECULAR CHAIN-LENGTH. R. S. Higginbotham and W. A. Richardson. *J. Soc. Chem. Ind.*, 1938, V. 57, P. 234–40; abs. in *J. T. I.*, Nov. 1938, P. A703. (C)

STARCH GRANULE: STRUCTURE. W. W. Lepeschkin. *Protoplasma*, 1938, V. 30, P. 309–10 (through *Chem. Zentr.*, 1938, ii, P. 1604); abs. in *J. T. I.*, Dec. 1938, P. A789.

If starch granules are cut up under cold water swelling does not take place, but this occurs if the starch is first ground in the dry state. Pasting

is accelerated more by citric and nitric acids than by hydrochloric acid. All types of starch are believed to contain the same polysaccharides. (C)

STATISTICAL MEASUREMENT OF VARIABILITY IN TEXTILE PRODUCTS. H. E. Daniels. *J. Huddersfield Text. Soc.*, 1937–38, pp. 18–20; abs. in *J. T. I.*, Dec. 1938, P. A767.

A short résumé of statistical methods likely to be of use in textile testing. (C)

TEXTILE MACHINES: CONSTRUCTION. P. Beckers. *Klepzig's Textil-Z.*, 1938, V. 41, P. 627–32; abs. in *J. T. I.*, March 1939, P. A193.

The author discusses problems of machine construction, such as dynamic stresses, groove effects and groove sensitivity, corrosion, durability, strength calculations, and arrangements for studying the distribution of stresses and measuring extensions, points out the need for the practical application of the results of general engineering research in the construction of textile machines, gives references to recent papers, and discusses textile machinery construction in relation to the German four-year plan. (C)

WOOL WAX. IV. TWO NEW ALCOHOLS IN WOOL WAX. V. METHOD OF ISOLATING CHOLESTEROL FROM WOOL WAX. T. Kuwata and M. Katuno. *J. Soc. Chem. Ind., Japan*, 1938, V. 41, P. 227–29 (through *C. A.*, 1938, V. 32, Col. 9536); abs. in *J. T. I.*, Feb. 1939, P. A142. (C)

Book Review

RAYON AND STAPLE FIBRE HANDBOOK. Herbert R. Mauersberger and Dr. E. W. K. Schwarz. Third Edition. 832 pp., illustrated. Rayon Handbook Co., New York, N. Y. Price $4.50 per copy in U. S. and Canada, $5.75 in other countries.

This is the third edition of this well-known Handbook, which has been completely revised, enlarged and brought up-to-date, as deemed necessary by the continued growth of the filament rayon industry, the tremendous progress of rayon staple fibre and spun rayons as well as the increased activity in research and technical knowledge. Two entirely new chapters are added namely: "The Manufacture of Rayon Staple Fiber and Spun Rayon Yarns" and a complete "Glossary of Rayon Terms." All other chapters have been considerably enlarged and new information added in all manufacturing subjects. These changes are so numerous that only a few of the more important ones can be mentioned. The authors have increased the number of special contributions from experts in respective and related fields such as Stanley B. Hunt, Textile Economics Bureau; H. B. Vollrath of the Viscose Process; Dr. Harold De Witt Smith on the Cellulose-Acetate Process; Theodore Wood on the Cuprammonium Process. There are also chapters written by Wm. H. Brown on Knitting, Dr. Erwin J. Saxl on Testing, C. C. Hubbard on Drycleaning, Geo. H. Johnson on Laundering, Leone Ann Heuer on Home and Consumer problems, a new feature. Photomicrographs of all rayon staple fibres were made for this book exclusively by Werner Von Bergen. The book serves as a complete, well-illustrated reference work on all phases of rayon production, manufacture and use, not only for the textile trade, but also for the student, economist and consumer. (C)